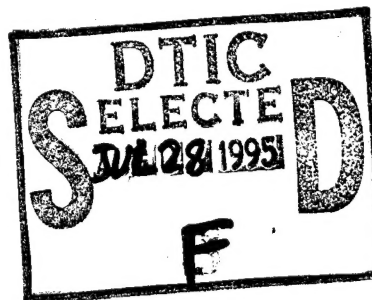


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Spectroelectrochemical Investigations of Molten Halide Solutions

June 14, 1995

Gleb Mamantov
Principal Investigator

26 JUN 1995

The main objective of this research, performed by Ellen Kurt Hondrogiannis, a graduate student at the University of Tennessee, was to investigate the utility of the combination of spectroscopy and electrochemistry, or spectroelectrochemistry (SEC), for studies of redox processes in molten halides. Three studies were done in the course of this work. A summary of each study follows.

The utilities of two fiber optic probing techniques, fiber optic cables connected to the dry box and a fiber optic probe for in situ studies, have been demonstrated. The Raman, UV-visible, and electron spin resonance (ESR) spectroelectrochemical behavior of chloranil in basic melt [<50 m/o AlCl_3] and the UV-visible and the ESR spectroelectrochemical behavior of chloranil in basic melt (<50 m/o AlCl_3) has been examined. The chloranil is electrochemically reduced in the basic melt via two one electron transfers. The results indicate that the radical anion intermediate exists as a complex with AlCl_3 (or Al_2Cl_7^-) in both basic and acidic melts.

UV-visible spectroscopic and spectroelectrochemical studies of NbCl_5 in the basic melt showed that a $\text{Nb}^{2.33+}$ cluster is electrochemically generated in the fourth reduction and that it is further generated chemically by the disproportionation reaction of Nb^{4+} , produced in the first wave, to Nb^{5+} and Nb^{3+} , the latter of which then decomposes to give the cluster. The cluster was shown to be less soluble at higher temperatures.

The UV-visible spectroscopic and spectroelectrochemical behavior of potassium hexachlororhenate (IV) was studied. The initial voltammograms show a new wave to grow in at a potential more positive than the $[\text{ReCl}_6]^{2-}$ reduction. The resulting voltammogram, consisting of three reduction and two oxidation waves, does not change further. Spectroelectrochemical results indicate that this first reduction is due to the $[\text{Re}_2\text{Cl}_8]^{2-}/[\text{Re}_2\text{Cl}_8]^{2-}$ couple. The second wave is believed to be due to the reductions of both $[\text{ReCl}_6]^{2-}$ and $[\text{Re}_2\text{Cl}_8]^{2-}$. The results are complicated by the instability of rhenium (III).

A list of publications resulting from this work is attached.

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E. M. Hondrogiannis and G. Mamantov, "Electrochemical and Spectroelectrochemical Investigation of K_2ReCl_6 and $[\text{Bu}_4\text{N}]_2\text{Re}_2\text{Cl}_8$ in the $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$ Melt", *Proceedings of the Ninth International Symposium on Molten Salts*, C. L. Hussey, D. S. Newman, G. Mamantov, and Y. Ito, eds., The Electrochemical Society, Inc., Pennington, NJ, 1994, pp. 521-524.

E. M. Hondrogiannis and G. Mamantov, "Spectroscopy, Electrochemistry, and Spectroelectrochemistry of Rhenium Chlorides in the $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$ Melt", accepted for publication by *J. Electrochem. Soc.*